भारतीय मानक
Indian Standard

IS 1448 [P : 84] : 2017

पेट्रौलियम और उसके उत्पादों के लिए परीक्षण के तरीके

[पी : 84] पेट्रौलियम उत्पादों में तत्वों का
पता लगाने के निर्धारण — आर्सेनिक

(पहला पुनरीक्षण)

Methods of Test for Petroleum and its Products

[P : 84] Determination of Trace Elements in
Petroleum Products — Arsenic

(First Revision)

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Methods of Test for Petroleum, Petroleum Products and Lubricants Sectional Committee, PCD 1

FOREWORD

This Indian Standard [P : 84] (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Test for Petroleum, Petroleum Products and Lubricants Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

This standard was originally published in 1975 which was adopted from International Series of Monographs on Analytical Chemistry, Volume 14 Analysis of Petroleum, for Trace Elements by O.T. Milner, published by PERGAMON PRESS, LONDON, 1963.In this revision precision statement has been modified.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 ‘Rules for rounding off numerical values (*revised*)’.

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 84] DETERMINATION OF TRACE ELEMENTS IN PETROLEUM PRODUCTS — ARSENIC

(First Revision)

1 SCOPE

This method is intended for the determination of arsenic in petroleum naphthas and other volatile distillates. The procedure is a rapid one and requires about 2 h in elapsed time. About 100 ml of sample is used and it is accurate over the range of 1 to 100 ppb.

2 OUTLINE OF THE METHOD

2.1 Arsenic in the sample is extracted with sulphuric acid and hydrogen peroxide. The extract is digested with hydrogen peroxide to destroy theorganic matter and the resulting solution is then transferred into an Erlenmeyer flask for arsine generation (*see* Fig. 1). Potassium iodide, stannouschloride and zinc are added and the arsine so evolved is then absorbed in silver diethyldithiocarbamate solution in pyridine. Arsenic forms a coloured complex with silver diethyldithiocarbamate and it is determinedcalorimetrically.

3 APPARATUS

3.1 Arsine Evolution Apparatus — consisting of evolution flask, hydrogen sulphide scrubber and arsine absorber as shown in Fig. 1.

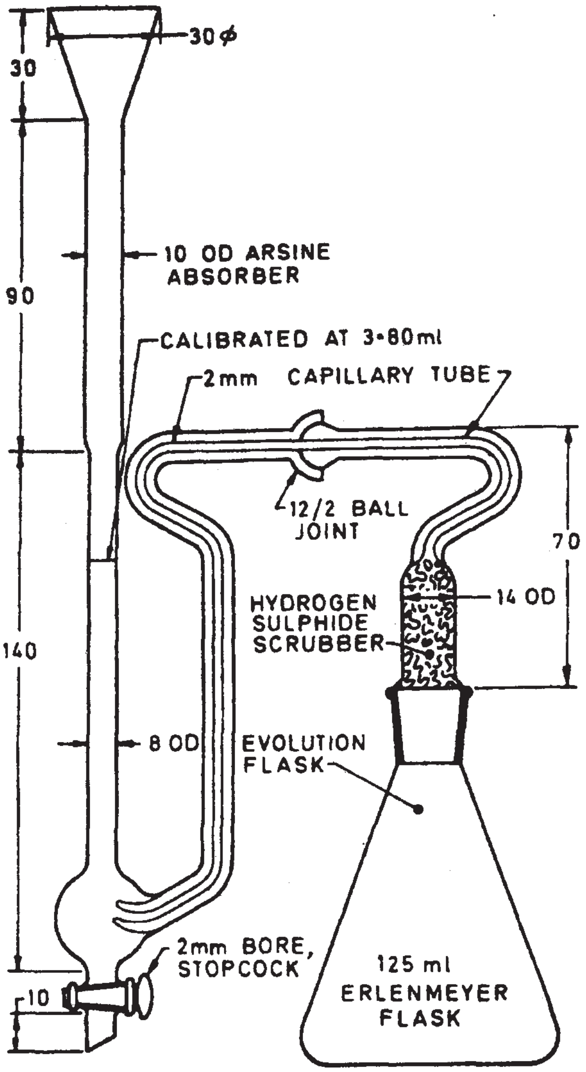
3.2 Spectrophotometer — capable of measuring absorbance in theregion of 540 nm and provided with matched cells of 70 mm. If decreasedsensitivity is required, ordinary 20 mm cells of 5 ml total capacity may beused; in this case the total volume of the absorbing solution is adjusted to 5.00 ml instead of 3.80 ml.

3.2.1 Alternatively, a suitable photoelectric colorimeter may be used in place of spectrophotometer.

3.3 Kjeldahl Flask — 500-ml capacity.

4 REAGENTS

4.1 Quality of Reagents — Unless otherwisespecified, pure chemicals and de-ionized water shall be used in the test. Water shall be de-ionized by passing through a mixed bed ion-exchanger.



Bring receiver close to evolution flask for stability.

All dimensions in millimetres.

FIG. 1 ARSINE EVOLUTION APPARATUS

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4.2 Sulphuric Acid — of 96 percent purity (relative density 1.84) having arsenic content 0.000 01 percent, *Max*.

4.3 Standard Arsenic Solution

4.3.1 *Standard Arsenic Solution (0.100 mg Arsenic per ml)* — Dissolve 0.132 g of arsenic trioxide in 2.5 ml of 20 percent sodium hydroxide, acidify with 2.5 ml of dilute sulphuric acid (1 : 5) and dilute to 1000 ml with water.

> *CAUTION* — Arsenic compounds are highly toxic. Do not apply mouth suction when pipetting solutions. Prevent contact with skin and eyes. Avoid inhalation of dusts and fumes.

4.3.2 *Dilute Standard Arsenic Solution* (0.1 µg *Arsenic per ml*) — Dilute 1 ml of standard arsenic solution (0.100 mg arsenic per ml) to 1 000 ml with water immediately before use.

4.4 Zinc Metal, Reagent Grade, Granular, 850-micron Size — Thearsenic content of this reagent varies widely. A lot containing preferably less than 0.3 µg per 5 g, as determined by blank runs with slightly varying amount of zinc, should be reserved for this determination.

4.5 Silver Diethyldithiocarbamate (AgDDC) — Prepare two solutions, one containing 1.7 g of silver nitrate in 100 ml of water and the other containing 2.3 g of sodium diethyldithiocarbamate in 100 ml of water. Cool below 20ºC and mix slowly with stirring. Filter off the lemon-yellow precipitate of silver diethyldithiocarbamate (AgDDC) and wash thoroughly with distilled water. Dry in a vacuum desiccator. The dry salt is stable at room temperature for at least six months. The reagent is also commercially available.

4.6 Silver Diethyldithiocarbamate Solution — Disslove 1.0 g of the salt in 200 ml of pyridine. Allow the solution to age for at least a week before use in order to ensure reproducible calibration. Alternatively, a calibration curve may be prepared at the time that unknown samples are analyzed. Once aged, the reagent will remain stable for several months.

4.7 Lead Acetate-Coated Glass Wool — Soak glass wool in 10 percent lead acetate solution, drain well, and dry. Store in a capped jar.

4.8 Stannous Chloride Solution — Dissolve 2 g of reagent in 10 ml of concentrated hydrochloric acid. Prepare fresh at least once a week.

4.9 Potassium Iodide — 15 percent solution.

4.10 Hydrogen Peroxide — 30 percent.

4.11 Pyridine

5 PROCEDURE

5.1 Add 15 ml of concentrated sulphuric acid and 20 ml of hydrogen peroxide to a 500 ml Kjeldahl flask containing one or two pumice stones, andcool to 0 to 5ºC. Add up to 100 ml of sample containing up to 1 µg of arsenic to the flask. Some samples, especially those which are high inolefins, react vigorously with the acid-peroxide mixture.Therefore, shakethe mixture gently at first. If a vigorous reaction is apparent or if thebottom of the flask heats up quickly, plunge the flask into ice water untilthe reaction subsides. If the mixture darkens at any time, add morehydrogen peroxide. Shake the mixture vigorously for 1 min, then refluxthe sample for half an hour with occasional shaking.

5.2 Cool the mixture, transfer it to a separatory funnel, and drain the acidlayer back into the Kjeldahl flask, washing the hydrocarbon layer oncewith 10 ml of water. With samples that do not char easily and withsamples of 10 ml or less, the separation may be eliminated and the organiclayer boiled away.

5.3 Heat the solution to sulphuric acid fumes, adding hydrogen peroxidewhen necessary to prevent excessive charring. Cool the solution, wash itinto an evolution flask, and adjust the total volume to 65 ± 5 ml. Coolthe solution to 20°C and add 1 ml of potassium iodide solution and, withswirling,5 or 6 drops of stannous chloride solution.Add 5.0 ± 0.1 g of zinc metal and immediately attach the hydrogen sulphide scrubber and theabsorber containing 3.80 ml of silver diethyldithiocarbamate (AgDDC) solution.

5.4 Allowthe evolution to proceed for 30 min, then detach theabsorber and dilute the solution again to exactly 3.80 ml with pyridine to replace what is lost during evolution.Pass a gentle air stream through the absorber for a few seconds to mix the solution.Immediately measure theabsorbance at 540 nm in the 70 mm cell; use silver diethyldithiocarbamate (AgDDC) solution as a reference.Convert the absorbance to µg (microgram) of arsenic by referring to a calibration curve that has beenprepared by evolving arsine from known amounts of arsenic in the range of 0.1 to 1 µg starting with 15 ml of sulphuric acid diluted to 65 ml.

6 CALCULATION AND REPORTING

6.1 Calculate the arsenic content as follows:

$$\text{Arsenic, parts per billon (ppb)} = \frac{M \times 10^3}{V \times D}$$

where

M = mass in µg (micrograms) of arsenic obtained from calibration curve after proper blank correction;

V = volume in ml of the sample taken for the analysis; and

D = relative density of the sample.

6.2 Report the result as arsenic content parts per billion.

7 PRECISION

7.1 Method precision shall be established based on round robin outcome.

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Amendments Issued Since Publication

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